

A STUDY OF THE PREPARATION OF THIOLBENZOIC ACID
AND BENZOYL DISULFIDE

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A THESIS
SUBMITTED FOR THE
DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

BY
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GEORGIA SCHOOL OF TECHNOLOGY
1932 .

M 65 Sept 33

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APPROVED, June 1, 1932

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of Doctor E. E. Reid, Professor of Chemistry, Johns-Hopkins University, at whose suggestion this research topic was undertaken. To Doctor B. B. Wroth and Doctor W. S. Taylor of the Department of Chemistry, Georgia School of Technology, he expresses his appreciation for their valuable suggestions and criticism.

A STUDY OF THE PREPARATION OF THIOLBENZOIC ACID AND BENZOYL DISULFIDE

Introduction

Thiolbenzoic acid (C_6H_5COSH) and its oxidation product, benzoyl disulfide ($C_6H_5COSSCOC_6H_5$), have long been known, but have been little worked on and deserve further study. Their preparation by simple methods would prove to be foundation for work on substituted thiolbenzoic acids. The purpose of this paper is to describe efforts toward production of these two substances by methods heretofore untried.

Thiolbenzoic Acid

Historical. -- Thiolbenzoic acid has been prepared by a wide variety of methods. The most important of these follow: (1) by the action of carbon oxysulfide on phenyl magnesium bromide in ether ¹; (2) by shaking a solution of benzoyl chloride in water-alcoholic potash with sulfur ²; (3) by boiling benzoic acid-phenyl ester or benzoic acid anhydride with alcoholic KSH ³; (4) by the action of benzoyl chloride on an alcoholic solution of K_2S ⁴; (5) by the action

(1) Weigert, Berichte der deutschen chemischen Gesellschaft, 36, 1010 (1903).

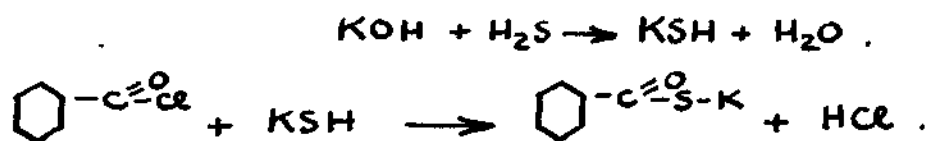
(2) Fromm, de Seixas Palma, Berichte, 39, 3324 (1906).

(3) Engelhardt, Latschinow and Malyschew, Zeitschrift fur Chemie, 1868, 354.

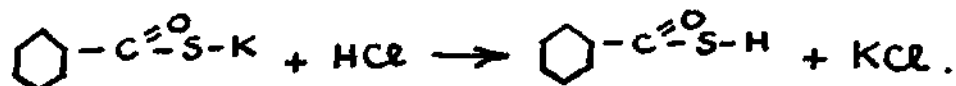
(4) Engelhardt, Latschinow and Malyschew, ibid., 355.

of benzoyl disulfide on alcoholic KSH ⁵ ; (6) by the action of a water solution of potash on a boiling alcoholic solution of benzoyl disulfide ⁶ ; (7) by dissolving benzoyl disulfide in an alcoholic solution of KSH ⁷ ; (8) on the addition of NH₃ to a solution of dibenzoyl disulfide in chloroform ⁸ ; (9) by the action of benzoyl chloride on an alcoholic solution of KSH, with subsequent acidification ⁹ .

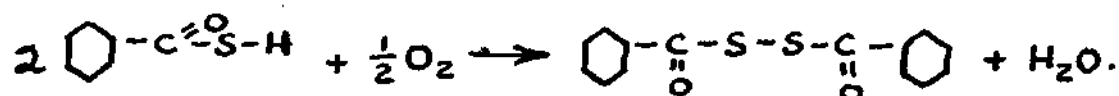
Experimental. -- The method of Kym ⁹ was followed in the preparation of thiolbenzoic acid for purposes of comparison. 20 gms. benzoyl chloride were added to a cold alcoholic solution of 20 gms. KOH saturated with H₂S, the precipitated KCl filtered off and the filtrate evaporated to dryness on a water bath. The yield of the reddish crude potassium thiolbenzoate, 27 gms., compared favorably with that of Kym. The salt was dissolved in the least possible amount of water and the free acid precipitated by the addition of 3N HCl. The equations are as follows:



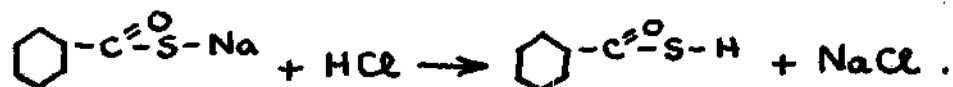
- (5) Engelhardt, Latschinow and Malyschew, *ibid.*, 357.
- (6) Fromm and Schmoldt, *Berichte*, 40, 2863 (1907).
- (7) Engelhardt, Latschinow and Malyschew, *ibid.*, 359.
- (8) Busch and Stern, *Berichte*, 29, 2150 (1896).
- (9) Kym, *Berichte*, 32, 3533 (1899), footnote.



It appears as a yellow oil which solidifies in the cold and melts at 24° . After cooling the solution, the solid was filtered off by suction. A difficulty is its ready oxidation in air to benzoyl disulfide, as shown by the equation:



There is no obvious reason for using the hydrosulfide instead of the more easily obtainable sulfide. Sodium salts are preferable to those of potassium. The alcohol is objectionable as it forms more or less ethyl benzoate. It was suggested that 350 gms. crystalline Na_2S be dissolved in 700 cc. H_2O and 140 gms. benzoyl chloride added, with intense mechanical stirring. On completion of this reaction the solution was acidified with HCl , when the thiolbenzoic acid should separate as a yellowish oil. The reactions are shown by the following equations:



Until the reaction worked well, only one-tenth of the above quantities were to be used.

A number of runs were made in an effort to carry out these reactions. The temperature was kept low in each case, the agitations being carried out between 0° and 40°C . At the

end of the agitation the solution was always of a reddish-yellow color and a small quantity of a yellowish oil settled to the bottom. Acidification, however, did not produce the thiolbenzoic acid sought except in traces. Varying either the acid or the strength of the acid used had no effect on the result. Since a 35% excess of Na_2S was used, the first action with the acid was the liberation of H_2S gas according to the equation:

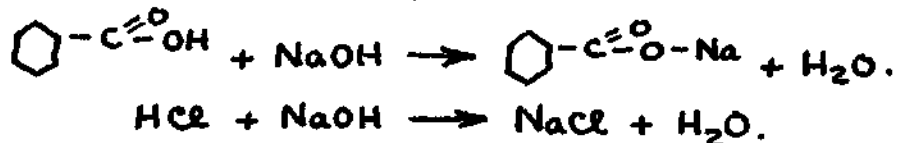


Addition of the acid to faint acidity produced no further visible change, while a large excess of acid yields a voluminous yellowish-white precipitate which had a melting point of $117-9^\circ$.

It was thought that this yellowish material was sulfur, since sulfur may have a melting point at practically any point between 113° and 120° , depending upon the form in which it is precipitated. Later conclusions led to the belief that it was very impure benzoyl disulfide (melting point, 128°), resulting from the rapid oxidation of any thiolbenzoic acid which was formed. An attempt was made to determine the exact nature of the material. Any benzoyl disulfide formed would have been contaminated with HCl , NaCl , and benzoic acid formed by hydrolysis of benzoyl chloride, indicated by the equation:



Treatment with NaOH would result in the formation of the soluble sodium benzoate and NaCl, as follows:



Subsequent washing with water should remove these soluble materials. However, on treatment with aqueous NaOH (3N) practically all of the unknown dissolved. This destroyed the belief that the material was benzoyl disulfide. Acidification of the solution resulted in the reprecipitation of the substance, which on further purification by repeated washing was identified by its appearance, chemical properties and melting point to be benzoic acid. The small amount of material unattacked by NaOH proved to be sulfur. Identical results were secured in every case.

Conclusions. -- Either thiolbenzoic acid was not formed in the reactions or the conditions were not favorable for its appearance. Instead of reacting with Na₂S present in the solution, the benzoyl chloride hydrolyzed, producing benzoic acid. Varying the temperature at which the reaction is carried out through the range of 0° to 40° had no effect on the final result. Further efforts to obtain thiolbenzoic acid by the proposed method were abandoned, repeated experiments having all led to the same conclusions.

Benzoyl Disulfide

Historical. -- Benzoyl disulfide has been prepared in a number of ways. Some of the most typical follow: (1) by the action of PbS on an ethereal solution of benzoyl chloride ¹⁰ ; (2) by boiling benzoyl chloride with sodium hydrosulfite ¹¹ ; (3) by the action of benzoyl chloride on N-N'-dimethyl thiuramdisulfide or N-N'-diethyl thiuramdisulfide in alcoholic-alkaline solution ¹² ; (4) by heating benzoic acid anhydride in a stream of dry H₂S at 130° ¹³ ; (5) by the oxidation of thiolbenzoic acid in ether ¹⁴ or CS₂ solution or in alcoholic solution ¹ in the air; (6) from potassium thiolbenzoate on treating a water solution with a solution of iodine in KI ¹⁰ or with excess CuSO₄ solution ¹⁰ , by treating a water solution with K₃Fe(CN)₆ ^{2, 15} , or by treating an alcoholic solution with FeCl₃ ¹⁰ .

Experimental. -- A new, more direct method was successfully utilized in the production of benzoyl disulfide. 24 gms. crystalline Na₂S·9H₂O were dissolved in 14 cc. H₂O, 32 gms. finely-powdered rhombic sulfur added, and the liquid warmed until all was dissolved, keeping from contact with air

(10) Engelhardt, Latschinow and Malyschew, *ibid.*, 358, 455.

(11) Bing and Marx, *Berichte*, 40, 3857 (1907).

(12) von Braun, *Berichte*, 36, 2272 (1903).

(13) Mosling, *Liebig's Annalen der Chemie*, 118, 304 (1).

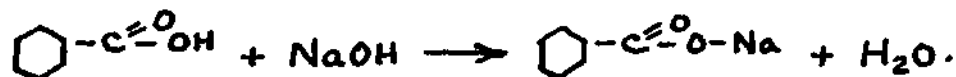
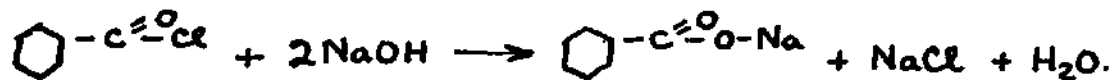
(14) Cloez, *Annalen*, 115, 27 (1).

(15) Fromm and Schmoldt, *ibid.*, 2862.

insofar as possible. This gives a reddish solution of Na_2S_2 . The solution was cooled to 5° and 26 gms. benzoyl chloride added, with intense mechanical stirring. A yellowish solid resembling sulfur very closely separated out at once. This solid dissolves in any excess benzoyl chloride which escapes hydrolysis to form a pasty mass or separates out if hydrolysis is complete.

The pasty mass is a source of trouble whenever it appears. It was thought advisable first to dilute the benzoyl chloride with several volumes of carbon disulfide in order to keep the materials liquid, benzoyl disulfide being very soluble in CS_2 ¹⁰. When all of the benzoyl chloride had dissolved, the heavier carbon disulfide layer was separated and evaporated to dryness on a water bath. However, difficulty was encountered in the operation because of the extreme inflammability of the carbon disulfide. Even when all the carbon disulfide has been vaporized, the excess benzoyl chloride remaining is very difficult to remove. The solid-liquid mixture now present is the same as that which would be secured if no carbon disulfide had been present when the initial reaction was carried out. Accordingly, the reaction was carried out with no carbon disulfide being added to the entering benzoyl chloride. Aqueous NaOH was used in the separation of the resulting materials. The benzoyl disulfide secured will be very impure. Excess benzoyl chloride, any unused Na_2S , and possibly some sulfur which might be set free during the course of the reaction, will be mixed with and adsorbed by the benzoyl disulfide. With NaOH,

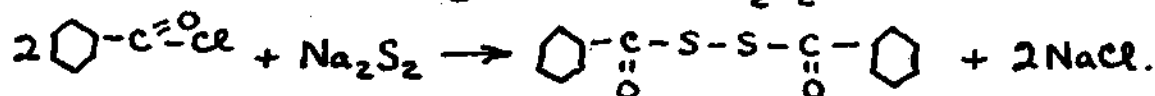
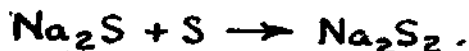
the benzoyl chloride and benzoic acid were converted into the water-soluble sodium benzoate. The following equations explain the reactions:



Filtration and washing with water will aid in the purification of the crude benzoyl disulfide.

An agitation with no carbon disulfide being present gave a solid material whose melting point was $117-8^\circ \text{C}$. Treatment with aqueous (3N) NaOH in the manner described immediately above increased the purity of the substance to such an extent that the melting point was elevated to 123° . Sulfur and benzoyl disulfide are the only solids of the general appearance and properties of the unknown material that could conceivably be present; the highest melting point that is possessed by any form of sulfur is 120° , whereas the melting point of benzoyl disulfide has been reported as 128° ^{1, 10}. Benzoyl sulfide, $\text{C}_6\text{H}_5\text{COSCOC}_6\text{H}_5$, and thiolbenzoic acid, $\text{C}_6\text{H}_5\text{COSH}$, are automatically eliminated because their melting points are 48° ⁴ and 24° ³, respectively. Repeated treatment (three additional digestions) with NaOH increased the melting point of the solid to 128° (cor.), the previously reported temperature given as the melting point of the pure substance. The pure benzoyl disulfide is of a pale yellowish-white color, a much lighter tint than that of sulfur. Thus it has been proved

that the reactions must proceed according to the equations:



To confirm the presence of benzoyl disulfide, the solid secured was submitted to a careful analysis for sulfur content. A combustion in a Parr bomb was carried out according to the standard method. Sulfur was oxidized to SO_4 and precipitated as BaSO_4 . The precipitate was filtered off, using a Gooch crucible with an asbestos mat, and ignited to constant weight. The crucible having previously been heated to constant weight, the percentage of sulfur was calculated. The equations explaining the method are:



A blank run was made to determine the percentage of sulfur in the reagents used. Then a combustion analysis was made, using the material thought to be benzoyl disulfide. The results are summarized in the table below:

No.	Sample	Wt. Sample	Orig. Wt. Crucible	Final Wt. Crucible
1	Blank No. 1	-----	16.5400 gm.	16.5450 gm.
2	Blank No. 2	-----	17.3615 "	17.3668 "
3	Benzoyl di- sulf. No. 1	0.3134 gm.	18.3040 "	18.8495 "
4	Benzoyl di- sulf. No. 2	0.3050 "	16.9854 "	17.5145 "

No.	Wt. BaSO ₄ Ppt.	Corrected Wt. Ppt.	Percent from Data	Theoretical Percent
1	0.0050 gm.	-----	-----	-----
2	0.0053 "	-----	-----	-----
3	0.5455 "	0.5403 gm.	23.69%	23.36%
4	0.5291 "	0.5239 "	23.60%	23.36%

It will be noted that comparable checks were obtained. The average of the two samples of the supposed benzoyl disulfide, 23.65%, is 0.39% higher than the theoretical, but is close enough to show beyond doubt that the material actually is benzoyl disulfide.

A series of runs have been made to determine the optimum temperature for the reaction used in the production of benzoyl disulfide. The same quantities of materials were used as above. The results are as follows:

Temp.	Wt. crude benz. dis.	M.P. crude benz. dis.	Wt. pure benz. dis. (M.P. 127-8°)	Theoretical yield	% yield
0°	18.97 gm.	118°	13.98 gm.	25.43 gm.	55%
10°	22.26 "	116°	14.82 "	25.43 "	58%
20°	34.90 "	114°	16.04 "	25.43 "	63%
30°	31.31 "	115°	18.81 "	25.43 "	74%
40°	28.68 "	114°	13.26 "	25.43 "	52%
50°	20.78 "	113°	10.95 "	25.43 "	43%
60°	24.87 "	111°	10.17 "	25.43 "	40%
70°	22.48 "	109°	7.19 "	25.43 "	28%
80°	22.39 "	110°	6.62 "	25.43 "	26%

Temp.	Wt. crude benz. dis.	M.P. crude benz. dis.	Wt. pure benz. dis. (M.P. 127-8°)	Theoretical yield	% yield
90°	12.62 gm.	112°	5.87 gm.	25.43 gm.	23%
100°	11.71 "	112°	4.33 "	25.43 "	17%

From the percentage yields it is obvious that the temperature most favorable to the reaction is in the neighborhood of 30°. Of course the weight of the crude benzoyl disulfide secured in each instance is necessarily a variable quantity and cannot be used in estimating the extent to which the reaction goes to completion.

Conclusions. -- Benzoyl disulfide has been prepared by the action of benzoyl chloride on an aqueous solution of sodium disulfide. The crude material must be carefully purified by repeated digestions with aqueous NaOH. The optimum temperature for the reaction has been found to be about 30° C.

Suggestions for Further Work

The method outlined above has given us a good method for the direct preparation of benzoyl disulfide. This has never been reduced to thiolbenzoic acid, but it should not be difficult. It was planned to carry out a series of reductions, the results to be incorporated in this paper, but lack of time forced its postponement.

It is suggested that iron turnings or iron powder be used with dilute acetic acid or sulfuric acid, and

granulated zinc and tin with the same acids. An alkaline reducing mixture to be employed might be zinc and caustic soda. Another excellent reducing agent is arsenious acid with an excess of rather strong caustic soda.